(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
7 August 2003 (07.08.2003)

PCT

(10) International Publication Number
WO 03/064767 A1

(51) International Patent Classification[7]: D21H 21/16, 17/71, 21/10 // 17/42, 17/44

(21) International Application Number: PCT/SE03/00112

(22) International Filing Date: 22 January 2003 (22.01.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02445012.4 31 January 2002 (31.01.2002) EP

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/064767 A1

(54) Title: PROCESS FOR MANUFACTURING PAPER

(57) Abstract: The invention relates to a process for manufacturing paper and board comprising providing a suspension comprising cellulosic fibres and at least a sizing agent, dewatering said suspension thereby forming a paper-web, whereby an aromatic-containing cationic vinyl addition polymer, and an anionic polymer having a weight average molecular weight in the range of from 6,000 up to about 100,000 selected from the group consisting of vinyl addition polymers and condensation polymers is added to the suspension.

Process for manufacturing paper

The present invention refers to a process for manufacturing paper and board comprising the addition of two different polymers to an aqueous cellulose-containing suspension one being an aromatic-containing cationic vinyl addition polymer and the other an anionic polymer having a weight average molecular weight in the range of from about 6,000 up to about 100,000 selected from the group consisting of vinyl addition polymers and condensation polymers.

Background

Internal sizing agents are usually added to the wet end of the paper making process whereby the adsorption capability of the paper of liquids is decreased. Commonly used internal sizing agents are sizing agents based on rosin derivatives and cellulose-reactive sizing agents, notably ketene dimers and acid anhydrides. Multipurpose office paper need to be rather heavily sized in order to function properly in today's high speed reproducing machines. One way of attaining paper which is fully sized, i.e. having a $cobb_{60}$ number below 30 or measuring the contact angle of a water droplet on the paper where angles larger the 80 degrees after 10 seconds indicate good sizing, is to add more sizing agent to the suspension. However, the likelihood of ending up with runability problems in the paper mill increases as well as the production costs.

Apart from the addition of sizing agents to the pulp suspension, dewatering and retention agents are also added to the suspension. As the name indicates, the latter agents enhance both dewatering and retention of the pulp suspension. According to the present invention it has surprisingly been found that sizing efficiency is improved by the addition of at least two different types of polymers to the pulp suspension which polymers simultaneously function as dewatering and retention agents. Thus, by applying the present process both sizing, dewatering and retention are positively influenced. The effect is also observed on suspensions having high conductivities.

According to the present invention it has been found that specifically improved sizing can be obtained by a process for manufacturing paper and board comprising providing a suspension comprising cellulose and at least a sizing agent, dewatering said suspension thereby forming a paper-web, whereby an aromatic-containing cationic vinyl addition polymer, and an anionic polymer having a weight average molecular weight in the range of from about 6,000 up to about 100,000 selected from the group consisting of vinyl addition polymers and condensation polymers vinyl addition polymer are added to the suspension.

Detailed description of the invention

The present invention is not restricted to specific types of cellulose suspensions, but can be applied on cellulose suspensions containing virgin or recycled pulp and

different fillers such as calcium carbonate. The pH of the suspension may also vary from being acidic, which is the case if sizing agents derived from rosins are used, to being neutral or alkaline. If cellulose-reactive sizing agents are used the pH of the cellulose suspension is neutral to alkaline, i.e. in the range from about 5 up to about 10, which also makes it possible to include inorganic filler materials in the suspension, e.g. precipitated calcium carbonate and clays. The two different polymers are suitable added to a fairly diluted lignocellulose-containing suspension commonly referred to as the thin stock having a concentration of from 0.1 up to 3.0 % by weight based on dry fibres.

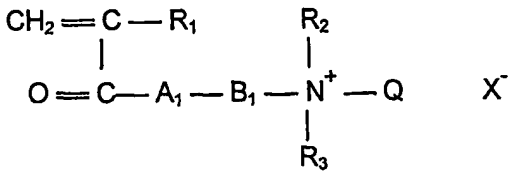
The process is furthermore not dependent on the type of sizing agent added, thus, any sizing agent or mixture of sizing agents may be present in the cellulose suspension. Preferably, the cellulose suspension contains cellulose-reactive sizing agents, normally present in an amount of from 0.01 to 5 % by weight based on dry fibres, and has a pH value where the cellulose-reactive sizing agent still functions properly, i.e. a pH in the range from 5 up to 10. Suitable cellulose-reactive sizing agents are ketene dimers, ketene multimers, acid anhydrides, organic isocyanates, carbamoyl chlorides and mixtures thereof, where ketene dimers and acid anhydrides are preferred.

According to the present process an aromatic-containing cationic vinyl addition polymer and an anionic vinyl addition polymer having a weight average molecular weight in the range of from about 6,000 up to about 100,000 is added to the cellulose suspension. Usually, the cationic polymer is added to the suspension prior to the addition of the anionic polymer. Suitably, the addition of the cationic polymer is followed by a shear stage or stages, whereas the anionic polymer is added after any stage providing significant shear but before the formation of the paper web.

Aromatic-containing cationic vinyl addition polymer

The aromatic-containing cationic vinyl addition polymer may be linear or branched and contain monomers having anionic or potentially anionic groups as long as the overall charge of the polymer is cationic. However, the cationic polymer is preferably obtained by polymerising a reaction mixture essentially free from monomers having anionic groups or groups which can be rendered anionic in aqueous compositions. The cationic polymer can be a homo polymer or a copolymer containing cationic aromatic monomers, cationic non-aromatic monomers and non-ionic monomers, the latter also being non-aromatic. Suitably, the cationic vinyl addition polymer contains cationic aromatic monomers selected from the group consisting of acrylamide, (meth)acrylamide, acrylate and (meth)acrylate, whereby said cationic monomers preferably have at least one aromatic group covalently linked to a nitrogen atom either direct or via hydrocarbon groups which can have heteroatoms. Preferably, the aromatic-containing cationic vinyl addition polymer contains aromatic (meth)acrylamide and/or (meth)acrylate monomers

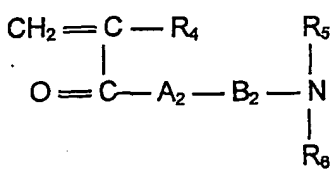
which are present in the polymer in an amount from about 2 molar % up to about 97 molar %. The aromatic-containing cationic vinyl addition polymer is suitably obtained by polymerising a cationic monomer or a reaction mixture containing a monomer mixture comprising a cationic monomer represented by the general formula (I):



(I)

wherein R_1 is H or CH_3; R_2 and R_3 are independently from another a hydrogen or an alkyl group having from 1 to 3 carbon atoms, usually 1 to 2 carbon atoms; A_1 is O or NH; B_1 is an alkylene group having from 2 to 8 carbon atoms, suitably from 2 to 4 carbon atoms, a hydroxy propylene group or a hydroxy ethylene group; Q is a substituent containing an aromatic group, suitably a phenyl or substituted phenyl group, which can be attached to the nitrogen by means of an alkylene group usually having from 1 to 3 carbon atoms, suitably 1 to 2 carbon atoms, and preferably Q is a benzyl group ($-CH_2-C_6H_5$); and X^- is an anionic counterion, usually a halide like chloride. Examples of suitable monomers represented by the general formula (I) include quaternary monomers obtained by treating dialkylaminoalkyl (meth)acrylates, e.g. dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate and dimethylaminohydroxypropyl (meth)acrylate, and dialkylaminoalkyl (meth)acrylamides, e.g. dimethylaminoethyl (meth)acrylamide, diethylaminoethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide, and diethylaminopropyl (meth)acrylamide, with benzyl chloride. Preferred cationic monomers of the general formula (I) include dimethylaminoethylacrylate benzyl chloride quaternary salt, dimethylaminoethylmethacrylate benzyl chloride quaternary salt and dimethylaminopropyl(meth)acrylamide benzyl chloride quaternary salt.

The cationic vinyl addition polymer can be a homopolymer prepared from a cationic monomer having an aromatic group or a copolymer prepared from a monomer mixture comprising a cationic monomer having an aromatic group and one or more copolymerizable monomers. Suitable copolymerizable non-ionic monomers include monomers represented by the general formula (II):

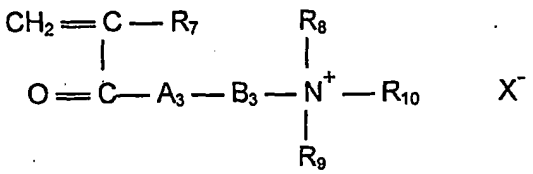


(II)

wherein R_4 is H or CH_3; R_5 and R_6 are each H or a hydrocarbon group, suitably alkyl, having from 1 to 6, suitably from 1 to 4 and usually from 1 to 2 carbon atoms; A_2 is O or NH; B_2 is

an alkylene group of from 2 to 8 carbon atoms, suitably from 2 to 4 carbon atoms, or a hydroxy propylene group or, alternatively, A and B are both nothing whereby there is a single bond between C and N (O=C — NR_5R_6). Examples of suitable copolymerizable monomers of this type include (meth)acrylamide; acrylamide-based monomers like N-alkyl (meth)acrylamides and N,N-dialkyl (meth)acrylamides, e.g. N-n-propylacrylamide, N-isopropyl (meth)acrylamide, N-n-butyl (meth)acrylamide, N-isobutyl (meth)acrylamide and N-t-butyl (meth)acrylamide; and dialkylaminoalkyl (meth)acrylamides, e.g. dimethylaminoethyl (meth)acrylamide, diethylaminoethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide and diethylaminopropyl (meth)acrylamide; acrylate-based monomers like dialkylaminoalkyl (meth)acrylates, e.g. dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, t-butylaminoethyl (meth)acrylate and dimethylaminohydroxypropyl acrylate; and vinylamides, e.g. N-vinylformamide and N-vinylacetamide. Preferred copolymerizable non-ionic monomers include acrylamide and methacrylamide, i.e. (meth)acrylamide, and the main polymer is preferably an acrylamide-based polymer.

Suitable copolymerizable cationic monomers include the monomers represented by the general formula (III):



(III)

wherein R_7 is H or CH_3; R_8 and R_9 are preferably a hydrocarbon group, suitably an alkyl group having from 1 to 3 carbon atoms; R_{10} can be a hydrogen or preferably a hydrocarbon group, suitably an alkyl group having from 1 to 8 carbon atoms, usually 1 to 2 carbon atoms; A_3 is O or NH; B_3 is an alkylene group of from 2 to 4 carbon atoms, suitably from 2 to 4 carbon atoms, or a hydroxy propylene group, and X^- is an anionic counterion, usually methylsulphate or a halide like chloride. Examples of suitable cationic copolymerizable monomers include acid addition salts and quaternary ammonium salts of the dialkylaminoalkyl (meth)acrylates and dialkylaminoalkyl (meth)acrylamides mentioned above, usually prepared using acids like HCl, H_2SO_4, etc., or quaternizing agents like methyl chloride, dimethyl sulphate, etc.; and diallyldimethylammonium chloride. Preferred copolymerizable cationic monomers include dimethylaminoethyl (meth)acrylate methyl chloride quaternary salt, diallyldimethylammonium chloride and and dimethylaminopropyl(meth)acrylamide benzyl chloride quartenary salt. Copolymerizable anionic monomers like acrylic acid, methacrylic acid, itaconic acid, various sulfonated vinyl addition monomers, etc. can also be employed and, preferably, in minor amounts.

The cationic vinyl addition polymer can be prepared from a monomer mixture generally comprising from 1 to 99 mole%, suitably from 2 to 50 mole% and preferably from 5 to 20 mole% of cationic monomer having an aromatic group, preferably represented by the general formula (I), and from 99 to 1 mole%, suitably from 98 to 50 mole%, and preferably from 95 to 65 mole% of other copolymerizable monomers which preferably comprises acrylamide or methacrylamide ((meth)acrylamide), the monomer mixture suitably comprising from 98 to 50 mole% and preferably from 95 to 80 mole% of (meth)acrylamide, the rest up to 100% preferably of compounds according to formula I and II.

Alternatively the cationic polymer can be a polymer subjected to aromatic modification using an agent containing an aromatic group. Suitable modifying agents of this type include benzyl chloride, benzyl bromide, N-(3-chloro-2-hydroxypropyl)-N-benzyl-N,N-dimethylammonium chloride, and N-(3-chloro-2-hydroxypropyl) pyridinium chloride. Suitable polymers for such an aromatic modification include vinyl addition polymers. If the polymer contains a tertiary nitrogen which can be quaternized by the modifying agent, the use of such agents usually results in that the polymer is rendered cationic. Alternatively, the polymer to be subjected to aromatic modification can be cationic, for example a cationic vinyl addition polymer.

Usually the charge density of the cationic polymer is within the range of from 0.1 to 6.0 meqv/g of dry polymer, suitably from 0.2 to 4.0 and preferably from 0.5 to 3.0. The weight average molecular weight of the cationic polymer is usually at least about 500,000, suitably above about 1,000,000 and preferably above about 2,000,000. The upper limit is not critical; it can be about 30,000,000, usually 20,000,000 and suitably 10,000,000.

The cationic vinyl addition polymer can be added into the suspension in amounts which can vary within wide limits depending on, inter alia, type of suspension, salt content, type of salts, filler content, type of filler, point of addition, etc. Generally the cationic vinyl addition polymer is added in an amount that give better sizing, dewatering and retention than is obtained when not adding it provided the anionic vinyl addition polymer is added. The cationic polymer is usually added in an amount of at least 0.002%, often at least 0.005% by weight, based on dry pulp, whereas the upper limit is usually 1.0% and suitably 0.5% by weight.

Anionic vinyl addition polymer

Further to the above described aromatic-containing cationic vinyl addition polymer, an anionic polymer having a weight average molecular weight in the range of from about 6,000 up to about 100,000 selected from the group consisting of vinyl addition polymers and condensation polymers is added to the cellulose suspension. The anionic polymer can be linear, branched or cross-linked, yet suitably essentially linear, and usually

water-soluble or water-dispersable. The anionic polymer may furthermore be a homopolymer or a copolymer containing at least two different types of monomers. Preferably, the anionic polymer is a vinyl addition polymer having a weight average molecular weight in the range of from about 6,000 up to about 100,000. Suitable anionic vinyl addition polymers are polymers obtained from a reaction mixture comprising vinylic unsaturated monomers, preferably vinylic unsaturated aromatic containing monomers, having one or more anionic groups or groups rendered anionic in aqueous solutions, suitably at least one sulphonate group. Examples of anionic groups attached to vinylic unsaturated monomers are phosphate groups, phosphonate groups, sulphate groups, sulphonic acid groups, sulphonate groups, carboxylic acid groups, carboxylate groups such as acrylic acid, methacrylic acid, ethyl acrylic acid, crotonic acid, itaconic acid, maleic acid or salts thereof, alkoxide groups, maleic acid groups and phenolic groups, i.e. hydroxy-substituted phenyls and naphthyls. Groups carrying an anionic charge are usually salts of an alkali metal, alkaline earth or ammonia. The anionic vinyl addition polymer may also in some extent contain cationic groups such as monomers having cationic groups, though, preferable the only ionic groups present in the vinyl addition polymer are anionic. Preferably, the anionic groups are linked to aromatic vinylic (ethylenically) unsaturated monomers such as styrene, i.e. styrene sulphonate. If the anionic vinyl addition polymer is a copolymer, said polymer can be obtained from a reaction mixture comprising non-ionic vinylic unsaturated monomers, e.g. acrylamide, (meth)acrylamide. The anionic vinyl addition polymer may comprise from about 20 mole % up to about 100 mole % of anionic monomers containing at least one anionic charge.

Suitable anionic condensation polymers having a weight average molecular weight in the range of from about 6,000 up to about 100,000 are condensates of an aldehyde such as formaldehyde with one or more aromatic compounds containing one or more anionic groups, and optional other co-monomers useful in the condensation polymerization such as urea and melamine. Examples of suitable aromatic compounds containing anionic groups comprises benzene and naphthalene-based compounds containing anionic groups such as phenolic and naphtholic compounds, e.g. phenol, naphthol, resorcinol and derivatives thereof, aromatic acids and salts thereof, e.g. phenylic, phenolic, naphthylic and naphtholic acids and salts, usually sulphonic acids and sulphonates, e.g. benzene sulphonic acid and sulphonate, xylen sulphonic acid and sulphonates, naphthalene sulphonic acid and sulphonate, phenol sulphonic acid and sulphonate. Examples of suitable anionic condensation polymers include anionic benzene-based and naphthalene-based condensation polymers, preferably naphthalene-sulphonic acid based and naphthalene-sulphonate based condensation polymers.

The weight average molecular weight of the anionic vinyl addition polymer and the condensation polymer is in the range of from about 6,000 up to about 100,000. The lower limit is suitably from about 7,000, preferably from about 8,000, preferably from about 15,000, preferably from about 25,000, whereas he upper limit is suitably up to about 80,000, preferably up to about 75,000, preferably up to 45,000, preferably up to about 40,000. Any combination of lower and higher limit can be a preferred range. If the anionic polymer is a vinyl addition polymer, the preferred ranges of the weight average molecular weight is from about 10,000 up to about 100,000, more preferably from about 15,000 up to about 75,000, most preferably from about 25,000 up to about 45,000.

The anionic polymer can have a degree of anionic substitution (DS_A) varying over a wide range dependent on, inter alia, the type of polymer used; DS_A is usually from 0.01 to 2.0, suitably from 0.02 to 1.8 and preferably from 0.025 to 1.5; and the degree of aromatic substitution (DS_Q) can be from 0.001 to 1.0, usually from 0.01 to 1.0, suitably from 0.02 to 0.7 and preferably from 0.025 to 0.5. In case the anionic polymer contains cationic groups, the degree of cationic substitution (DS_C) can be, for example, from 0 to 0.2, suitably from 0 to 0.1 and preferably from 0 to 0.05, the anionic polymer having an overall anionic charge. Usually the anionic charge density of the anionic polymer is within the range of from 0.1 to 6.0 meqv/g of dry polymer, suitably from 0.5 to 5.0 and preferably from 1.0 to 5.0.

The anionic polymer can be added to the suspension in amounts which can vary within wide limits depending on, inter alia, type of stock, salt content, type of salts, filler content, type of filler, point of addition, etc. Generally the anionic polymer is added in an amount that give better sizing, dewatering and retention than is obtained when not adding the anionic polymer provided the cationic vinyl addition polymer is added. The anionic polymer is usually added in an amount of at least 0.001%, often at least 0.005% by weight, based on dry pulp, whereas the upper limit is usually 3.0% and suitably 1.0% by weight.

According to one preferred embodiment of the present invention the aromatic-containing cationic vinyl addition polymer can be provided as an aqueous composition, suitably aqueous solution, preferably comprising further cationic polymers, for example synthetic cationic polymers and naturally occurring polymers. Suitable synthetic cationic polymers cationic are vinyl addition polymers such as acrylamide based polymers or acrylate based polymers. Other synthetic cationic polymers include cationic condensation polymers like epihalohydrin polymers, e.g. polymers formed by reacting aliphatic amines and epichlorohydrine, polyamideamine polymers, polyethyleneimine polymers. Preferred naturally occurring cationic polymers as cationic polysaccharides, particularly cationic starch and aromatic substituted cationic starch. The aqueous solution preferably contains the aromatic-containing cationic vinyl addition polymer in a predominant amount, i.e. at

least 50 % by weight, even though effects are present at considerably lesser amounts, down to amount at least 10 % by weight. The further cationic polymers referred to in this paragraph may also be added separately.

According to yet another preferred embodiment of the present invention inorganic anionic microparticulate materials like anionic silica-based particles, polysilicic acid and clays of the smectite type are added to the suspension. The inorganic anionic microparticulate material can be added separately to the suspension or is preferably comprised in an aqueous composition also comprising the anionic polymer.

Furthermore, the process can also be useful in the manufacture of paper and board from cellulosic suspensions having high conductivity. In such cases, the conductivity of the suspension that is dewatered on the wire is usually at least 1.0 mS/cm, suitably at least 2.0 mS/cm, and preferably at least 3.5 mS/cm. Conductivity can be measured by standard equipment such as, for example, a WTW LF 539 instrument supplied by Christian Berner. The values referred to above are suitably determined by measuring the conductivity of the cellulosic suspension that is fed into or present in the head box of the paper machine or, alternatively, by measuring the conductivity of white water obtained by dewatering the suspension. High conductivity levels mean high contents of salts (electrolytes) which can be derived from the materials used to form the stock, from various additives introduced into the stock, from the fresh water supplied to the process, etc. Further, the content of salts is usually higher in processes where white water is extensively recirculated, which may lead to considerable accumulation of salts in the water circulating in the process.

The invention is further illustrated in the following examples which, however, are not intended to limit the same. Parts and % relate to parts by weight and % by weight based on dry fibres, respectively, unless otherwise stated. All compound added to the furnish are calculated as dry material, if not otherwise indicated. In the examples, a good retention is shown by a low turbidity value in the white water, i.e. more fines and filler are retained in the formed sheet. A turbidity value under 120 is acceptable and a value under 90 is in this set of experiment excellent. The dewatering figure should also be low. The sizing of the paper was measured by the contact angle of a water droplet on the paper. Contact angles larger the 80 degrees after 10 seconds are indicating a good sizing.

Example 1

The pulp (at 3%) used was a 80/20 mixture of hardwood/softwood kraft. Ground calcium carbonate filler (GCC) was added to the pulp, to a filler concentration of 40% on dry solids. The resulting furnish was diluted to 0.3% before additional chemicals were added. The chemical additions are expressed as % on dry solids in the furnish.

In this example two furnishes were used one having a low conductivity of 500 μS/cm (furnish I), the other having a high conductivity of 4.0 μS/cm (furnish II). The conductivity was adjusted by addition of sodium sulphate. A dispersion containing a conventional ketene dimer sizing agent and 1% cationic starch were added to the furnishes. Subsequent to these additions, either 0.1% of an aromatic cationic polyacrylamide having benzyldimethylammonium groups (A-PAM) or 0.1% of a conventional non-aromatic cationic polyacrylamide (C-PAM) was added prior to the addition of either 0.1% of a silica sol or 0.1% of an anionic polystyrene sulphonate having a weight average molecular weight of 70,000 (PSS). The added amounts of compounds are indicated in table I and II. The retention and dewatering properties of the formed furnishes were evaluated by measuring the dewatering time using a Dynamic Drainage Analyser (DDA-unit). A lower value in this test means better dewatering efficiency. The retention was evaluated by measuring the turbidity of the white water with a Nephelometer 156 from Novasine. A lower turbidity value signifies higher retention of solids in the DDA-unit. Moreover, the sizing of the formed, dried and cured paper was evaluated by measuring the contact angle of water after 10 seconds utilising a Dynamic Absoption and contact angle tester from Fibro Systems (DAT). A higher value of the contact angle means better sizing efficiency.

Table I, Furnish II (high conductivity)

test	Amount of added ketene dimer/[kg/t dry pulp]	Type of cationic polyacrylamide	Type of anionic compound	Turbidity	Dewatering /[sec.]	Contact angle (10 sec./[degrees]
blank*	0.2	none	none	390	7.8	below 10
1	0.2	C-PAM	silica sol	91	6.92	29.6
2	0.2	A-PAM	PSS	47	4.54	44.6
3	0.3	C-PAM	silica sol	90	6.64	80.8
4	0.3	A-PAM	PSS	43	4.47	84.6
5	0.4	C-PAM	silica sol	90	6.77	89.9
6	0.4	A-PAM	PSS	47	4.47	94.4

As shown by table I, the addition of an aromatic-modified cationic vinyl addition polymer and an anionic vinyl addition polymer significantly increases not only dewatering and retention but also the sizing efficiency.

* No addition of neither cationic polyacrylamide nor anionic compound, otherwise conditions were the same as for tests 1 and 2.

Table II, Furnish I (low conductivity)

test	Amount of added ketene dimer/[kg/t dry pulp]	Type of cationic polyacrylamide	Type of anionic compound	Turbidity	Dewatering /[sec.]	Contact angle (10 sec./[degrees]
blank*	0.3	none	none	420	5.6	35
1	0.3	C-PAM	silica-sol	100	4.8	83.3
2	0.3	A-PAM	PSS	76	3.5	87.8

* In this test neither cationic polyacrylamide nor anionic compound was used, otherwise conditions were the same as for tests 1 and 2.

Example 2

The furnish used was the same as used in example 1, however, in this example the furnish was adjusted to a conductivity of 400 μS/cm

The sizing dispersion as used in example 1 was added to the furnish followed by the addition of cationic starch. The dosage for the size was 0.03% (calculated as active ketene dimer on dry furnish) and for the cationic starch 1.0%. Subsequent to these additions, 0.1% of an aromatic cationic polyacrylamide having benzyldimethylammonium groups was added prior to the addition of 0.07% of an anionic polystyrene sulphonate having different weight average molecular weights as indicated in table III and an anionic naphthalene sulphonate, respectively. The added amounts of compounds are indicated in table III. The retention and dewatering properties of the formed furnishes were evaluated by measuring the dewatering time using a DDA-unit. The retention was evaluated by measuring the turbidity of the white water with a Nephelometer 156 from Novasine. Moreover, the sizing of the formed, dried and cured paper was evaluated by measuring the contact angle of water after 10 seconds utilising a DAT equipment.

Table III

test	Weight average molecular weight of the anionic polymer	Turbidity	Dewatering/[sec.]	Contact angle (10 sec./[degrees]
blank*	none	125	5.4	below 30
1	8,000[2]	78	5.05	91
2	20,000[2]	75	4.95	94
3	35,000[1]	56	4.89	92.7
4	75,000[1]	50	4.03	88
5	100,000[1]	47	3.82	85
6	780,000[1]	30	3.17	69.2

1:polystyrene sulphonate, 2:naphthalene sulphonate

Tests 1 to 5 are according to the present invention, i.e. the anionic polymer having a weight average molecular weight in the range of from about 6,000 up to about 100,000. As can be seen in table III, the sizing efficiency is significantly increased while at the same time the turbidity and dewatering performance are high with regard to tests 1 to 5 compared to the blank. In addition, comparing test 6 with tests 1 to 5 (the latter five according to the invention), the sizing efficiency is much higher, while simultaneously the turbidity value still indicates good retention. What is more, a contacting angle of 69.2 as obtained in test 6 is not an acceptable sizing degree. Thus, the overall performance of tests 1 to 5 in respect of retention, dewatering and not least sizing clearly outperform test 6.

* No addition of neither cationic polyacrylamide nor anionic compound, otherwise conditions were the same as for tests 1 to 6.

Claims

1. A process for manufacturing paper and board comprising providing a suspension comprising cellulosic fibres and at least a sizing agent, dewatering said suspension thereby forming a paper-web, characterised in that to the suspension is added an aromatic-containing cationic vinyl addition polymer, and an anionic polymer having a weight average molecular weight in the range of from about 6,000 up to about 100,000 selected from the group consisting of vinyl addition polymers and condensation polymers.

2. A process according to claim 1, characterised in that the anionic polymer has a weight average molecular weight in the range from about 6,000 up to about 80,000.

3. A process according to any of the preceding claims, characterised in that the anionic polymer comprises aromatic monomers having sulphonate groups.

4. A process according to claim 1, characterised in that the anionic polymer is selected from the group of vinyl addition polymers.

5. A process according to claim 4, characterised in that the anionic vinyl addition polymer comprises aromatic monomers.

6. A process according to claim 5, characterised in that the aromatic monomers have at least one sulphonate group.

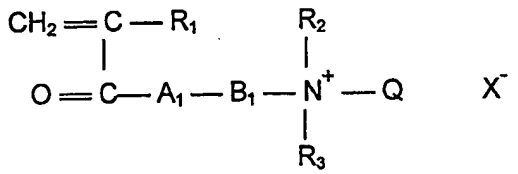
7. A process according to claim 4 , characterised in that the anionic vinyl addition polymer is polystyrene sulphonate.

8. A process according to any of the preceding claims, characterised in that the anionic polymer is added to the suspension in an amount from about 0.005 % by weight up to about 1.0 % by weight based on dry pulp.

9. A process according to any of the preceding claims, characterised in that the aromatic-containing cationic vinyl addition polymer has a weight average molecular weight of at least about 500,000.

10. A process according to claim 1, characterised in that the cationic vinyl addition polymer is prepared from a reaction mixture comprising from about 1 up to 99 mole% of a cationic monomer having an aromatic group.

11. A process according to claim 11, characterised in that the cationic monomer having an aromatic group is represented by formula (I)



(I)

wherein R_1 is H or CH_3; R_2 and R_3 are independently from another a hydrogen or an alkyl group having from 1 to 3 carbon atoms; A_1 is O or NH; B_1 is an alkylene group having from 2 to 8 carbon atoms; Q is a substituent containing an aromatic group; and X^- is an anionic counterion.

12. A process according to any of the preceding claims, characterised in that the aromatic-containing cationic vinyl addition polymer is added in an amount of from about 0.002 % by weight up to about 1.0 % by weight based on dry pulp.

13. A process according to claim 1, characterised in that the suspension comprising cellulosic fibres has a conductivity of at least about 1.0 mS/cm.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/SE 03/00112

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D21H21/16 D21H17/71 D21H21/10 //D21H17/42,D21H17/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents:

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"&" document member of the same patent family.

Date of the actual completion of the international search	Date of mailing of the international search report
16 April 2003	08/05/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Karlsson, L

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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